

Stochastic properties of systems controlled by autocatalytic reactions I

L. Pál*

KFKI Atomic Energy Research Institute H-1525 Budapest 114, POB 49 Hungary

We analyzed the stochastic behavior of systems controlled by autocatalytic reaction $A + X \rightarrow X + X$. Assuming the distribution of reacting particles in the system volume to be uniform, we introduced the notion of the point model of reaction kinetics, and derived a system of differential equations for probabilities of finding $n = 0, 1, \dots$ autocatalytic particles at a given time moment. It has been found that the kinetic law of the mass action cannot be supported by stochastic model.

PACS numbers: 02.50.Ey, 05.45.-a, 82.20.-w

Keywords: stochastic processes; autocatalytic reactions; lifetime

Introduction

The system denoted by \mathcal{S} is defined as an aggregation of particles capable for autocatalytic reactions. Symbols X and A are used for notations of *autocatalytic* and *substrate particles*, respectively. The system is "open" for particles A , when it is in contact with a large reservoir which keeps constant the number of particles A . In contrary, the system is "closed", when particles cannot be injected in or extracted from the system. We suppose that the system is always closed for the autocatalytic particles X .

As known, there are many papers and books [1, 2, 3, 4] dealing with the influence of spacial (mostly diffusive) motion of particles on the kinetics of reactions, however, in many cases the complexity of the problem did not allow to obtain exact results. In order to analyze one of the decisive factors determining the stochastic nature of autocatalytic reactions, in the present paper we do not deal with the diffusion of particles, instead we introduce the notion of *the point model of reaction kinetics*, similarly to that used in the theory of neutron chain reactors. It is to note that the point model of the reaction kinetics is based on a severe assumption according to that the reacting particles are distributed uniformly in the whole volume of the system. In this case, it can be stated that the probability of a reaction between two particles is proportional to the product of their actual numbers in the system. This approach is a highly simplified but useful model for systems, in which the number of particles is small, and the largest distant within the system is smaller than the characteristic length of interaction between the particles.

In the sequel we will study closed systems controlled by random process in which the *particles X catalyze the conversion of particles A into further X 's*. Changing adiabatically the number of particles A with help of a suitable reservoir, we can investigate the influence of the environment on the system behavior.

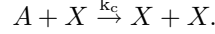
We say that a system is in a *living state* when the conditions for autocatalytic reactions are existing, while a system is in a *dead state* when there is no possibility for autocatalytic reactions. The random time spent by a system in the living state is *the lifetime of the system*. One of the aims of this paper is the determination of the probability distribution of the lifetime and the study of its random properties.

The organization of the paper as follows. To elucidate the approach that we will follow in the present work, in Section 1 we deal with systems controlled by the autocatalytic reaction $A + X \rightarrow X + X$. We derive and solve a system of differential equations determining the probabilities to find $n = 0, 1, \dots, N_A$ new X particles arisen from A particles during the time interval $(0, t)$. Since the system is closed, the number of particles A is decreasing with time, and finally becomes zero, i.e. the system reaches its dead state. By using the generating function equations, in Section 2 we show that the stochastic approach brings about an equation for the mean value of the number of autocatalytic particles completely different from the classical rate equation based on the kinetic law of the mass action. In order to obtain some kind of solution of the hierarchical equation system derived for moments, *the moment-closure (decoupling) approximation* has been applied by many authors [5, 6], however, the consequences of this procedure were hardly investigated. Since we succeeded to obtain exact results for the time dependence of moments, in Section 3 we analyzed the error caused by the decoupling approximation. Finally, in Section 4 we study the random properties of the system lifetime.

*Electronic address: lpal@rmki.kfki.hu

I. SYSTEMS CONTROLLED BY REACTION $A + X \rightarrow 2X$

We would like to study the properties of *closed systems* \mathcal{S} of constant volume V controlled by the reaction



Denote by N_A and N_X the numbers of particles A and X , respectively at time instant $t = 0$. As the particles X convert A into further X 's, so the number of particles A strictly decreases, and finally, the autocatalytic process is stopped. Obviously, in this case the system contains only X particles, and this is the state which is called *dead state*.

A. Kinetic rate equation

Denote by $m(t)$ the expectation value of the number of particles A converted into X during the time interval $[0, t]$. Obviously,

$$m_A(t) = N_A - m(t), \quad \text{and} \quad m_X(t) = N_X + m(t) \quad (1)$$

are the average number of particles A and X , respectively at the time moment $t \geq 0$. Introducing the notations

$$a(t) = \frac{m(t)}{V}, \quad c_A(0) = \frac{N_A}{V}, \quad \text{and} \quad c_X(0) = \frac{N_X}{V},$$

according to the kinetic law of mass action we can write the rate equation in the following form:

$$\frac{da(t)}{dt} = k_c [c_A(0) - a(t)] [c_X(0) + a(t)].$$

Taking into account the initial condition $a(0) = 0$, and using the abbreviation $u = k_c t/V$, one obtains that

$$a(u) = c_A(0) \frac{1 - e^{-N_0 u}}{1 + \rho e^{-N_0 u}}, \quad (2)$$

where

$$\rho = \frac{N_A}{N_X} \quad \text{and} \quad N_0 = N_A + N_X.$$

For the sake of comparison with the results of calculations of the stochastic model, let us introduce the ratios:

$$r_A(u) = \frac{m_A(u)}{N_A} = (1 + \rho) \frac{e^{-N_0 u}}{1 + \rho e^{-N_0 u}}, \quad (3)$$

and

$$r_X(u) = \frac{m_X(u)}{N_X} = (1 + \rho) \frac{1}{1 + \rho e^{-N_0 u}}. \quad (4)$$

B. Stochastic model

Denote the number of particles A converted into particles X during the time interval $[0, t]$ by the random function $\xi(t) \in \mathcal{Z}_+$, where \mathcal{Z}_+ is the set of nonnegative integers. At the same time, note that $\xi(t)$ is the number of new X particles appearing in $[0, t]$. Let

$$\mathcal{P}\{\xi(t) = n | \xi(t) = 0\} = p(t, n), \quad 0 \leq n \leq N_A \quad (5)$$

be the probability to find n new X particles at the time moment $t \geq 0$ in the system \mathcal{S} provided that at $t = 0$ the number of new particles X was zero and the system contained N_A particles of type A and N_X particles of type X . The pair of integers $\{N_A, N_X\}$ denotes the *initial state of the system* \mathcal{S} . Assume that $\alpha \Delta t + o(\Delta t)$ is the probability

that any of particles X brings about a reaction with any of particles A . If the numbers of A and X particles in the system at time instant $t \geq 0$ are $N_A - n$ and $N_X + n$, respectively, then

$$h_n \Delta t + o(\Delta t) = \alpha [N_A - n] [N_X + n] \Delta t + o(\Delta t) \quad (6)$$

is the probability that the reaction $A + X \xrightarrow{k_c} 2X$ is realized in the time interval $(t, t + \Delta t)$. It is to note that $\alpha = k_c/V$ and $h_{N_A} = 0$. By using the expression (6) one can write

$$p(t + \Delta t, n) = p(t, n)(1 - h_n \Delta t) + h_{n-1} p(t, n-1) \Delta t + o(\Delta t),$$

and obtain immediately the equation

$$\frac{dp(t, n)}{dt} = -h_n p(t, n) + h_{n-1} p(t, n-1), \quad 1 \leq n \leq N_A. \quad (7)$$

If $n = 0$, then

$$\frac{dp(t, 0)}{dt} = -h_0 p(t, 0), \quad (8)$$

and taking into account the initial condition $p(0, 0) = 1$ one has

$$p(t, 0) = e^{-h_0 t} = e^{-N_A N_X u}. \quad (9)$$

By introducing the Laplace transforms

$$U_n(s) = \int_0^\infty e^{-st} p(t, n) dt, \quad n = 1, 2, \dots, N_A,$$

since $p(0, n) = 0$, if $n > 0$, we obtain from Eq. (7) the recursive relation

$$(s + h_n) U_n = h_{n-1} U_{n-1}(s), \quad n > 0,$$

which can be easily solved by starting with

$$U_0(s) = \frac{1}{s + h_0}. \quad (10)$$

The solution can be written into the form:

$$U_n(s) = \frac{h_0 h_1 \cdots h_{n-1}}{(s + h_0)(s + h_1) \cdots (s + h_n)}, \quad n = 1, 2, \dots, N_A. \quad (11)$$

In order to obtain the probabilities $p(t, n)$, $1 \leq n \leq N_A$, the next step seems to be very simple: one has to expand $U_n(s)$ into the series of partial fractions, and then to perform the inverse Laplace transformation. However, the task is slightly more complex.

If $N_A - N_X = n_c \leq 0$, then it is obvious that the quantities h_0, h_1, \dots, h_n are all different and so, we can write

$$U_n(s) = \sum_{k=0}^n \frac{C_{nk}}{s + h_k}, \quad (12)$$

where

$$C_{nk} = \frac{h_0 h_1 \cdots h_{n-1}}{(h_0 - h_k)(h_1 - h_k) \cdots (h_{k-1} - h_k)(h_{k+1} - h_k) \cdots (h_n - h_k)}, \quad (13)$$

$$n = 1, 2, \dots, N_A \quad \text{and} \quad k = 0, 1, \dots, n,$$

and since $C_{00} = 1$, we obtain

$$p(t, n) = \sum_{k=0}^n C_{nk} e^{-h_k t}, \quad n = 0, 1, \dots, N_A. \quad (14)$$

If $N_A - N_X = n_c > 0$, then it can be easily proved the following statement: if n_c is even, i.e. $n_c = 2k_c$, then

$$h_{n_c} = h_0, h_{n_c-1} = h_1, \dots, h_{k_c+1} = h_{k_c-1},$$

while if n_c is odd, i.e. $n_c = 2k_c + 1$, then

$$h_{n_c} = h_0, h_{n_c-1} = h_1, \dots, h_{k_c+1} = h_{k_c}.$$

Let us denote the denominator of $U_n(s)$ by

$$V_n(s) = (s + h_0)(s + h_1) \cdots (s + h_n),$$

and introduce the notation

$$Q(j, s) = \prod_{i=0}^j (s + h_i)^2.$$

In the case of $n > n_c$ we can show that

$$V_n(s) = \begin{cases} Q(k_c - 1, s)(s + h_{k_c})(s + h_{n_c+1}) \cdots (s + h_n), & \text{if } n_c = 2k_c, \\ Q(k_c, s)(s + h_{n_c+1}) \cdots (s + h_n), & \text{if } n_c = 2k_c + 1, \end{cases}$$

while in the case of $n = n_c$ we obtain

$$V_{n_c}(s) = \begin{cases} Q(k_c - 1, s)(s + h_{k_c}), & \text{if } n_c = 2k_c, \\ Q(k_c, s), & \text{if } n_c = 2k_c + 1. \end{cases}$$

When $n < n_c$ and $0 < n \leq k_c$, then we have

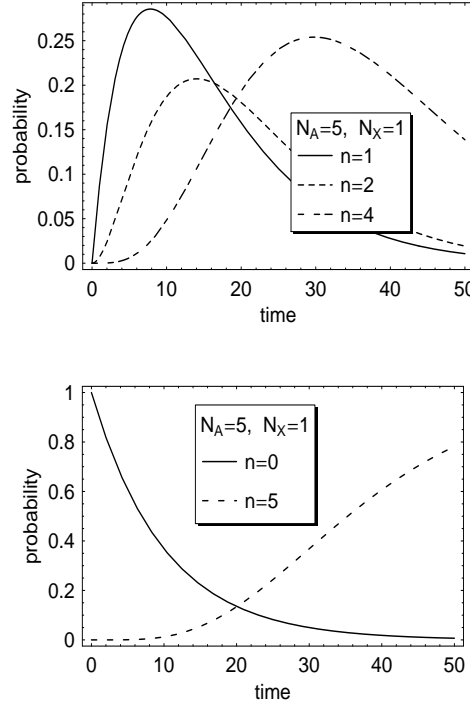


FIG. 1: Probabilities of finding $n = 0, 1, 2, 4, 5$ new X particles at time moment t provided that the initial state of the system was $\{5, 1\}$.

$$V_n(s) = \prod_{i=0}^n (s + h_i)$$

for both, even and odd values of n_c , but in the case of $k_c < n < n_c$ we should use the formula:

$$V_n(s) = \begin{cases} \prod_{i=0}^{n_c-n-1} (s + h_i) Q(n - k_c - 1, s)(s + h_{k_c}), & \text{if } n_c = 2k_c, \\ \prod_{i=0}^{n_c-n-1} (s + h_i) Q(n - k_c - 1, s), & \text{if } n_c = 2k_c + 1. \end{cases}$$

For the sake of illustration it seems to be useful to write down the equations of $U_n(s)$ when $N_A = 5$ and $N_X = 1$. One obtains

$$\begin{aligned} U_5(s) &= \frac{h_0^2 h_1^2 h_2}{(s + h_0)^2 (s + h_1)^2 (s + h_2) s}, & U_0(s) &= \frac{1}{s + h_0} \\ U_4(s) &= \frac{h_0 h_1^2 h_2}{(s + h_0)^2 (s + h_1)^2 (s + h_2)}, & U_1(s) &= \frac{h_0}{(s + h_0)(s + h_1)}, \\ U_3(s) &= \frac{h_0 h_1 h_2}{(s + h_0)(s + h_1)^2 (s + h_2)}, & U_2(s) &= \frac{h_0 h_1}{(s + h_0)(s + h_1)(s + h_2)}. \end{aligned}$$

One can see in FIG. 1 that the probability $p(t, n)$ versus t curves with exception of $n = 0$ and $n = 5$ have a well-defined maximum the location of which is increasing with t .

II. GENERATING FUNCTION EQUATION

In order to make easier the derivation of equations for moments of the random function $\xi(t)$ it is worthwhile to introduce the generating function

$$\tilde{g}(s, z) = \sum_{n=0}^{N_A} U_n(s) z^n. \quad (15)$$

It can be proved that $\tilde{g}(s, z)$ satisfies the following equation:

$$\alpha z^2 (1 - z) \frac{d^2 \tilde{g}(s, z)}{dz^2} - \alpha (n_c - 1) z (1 - z) \frac{d \tilde{g}(s, z)}{dz} - [s + h_0 (1 - z)] \tilde{g}(s, z) + 1 = 0. \quad (16)$$

In many cases the use of the exponential generating function

$$\tilde{g}_{exp}(s, y) = \sum_{n=0}^{N_A} U_n(s) e^{ny} \quad (17)$$

is more advantageous, therefore we write it down also:

$$\alpha (e^y - 1) \frac{d^2 \tilde{g}_{exp}(s, y)}{dy^2} - \alpha n_c (e^y - 1) \frac{d \tilde{g}_{exp}(s, y)}{dy} + [s - h_0 (e^y - 1)] \tilde{g}_{exp}(s, y) - 1 = 0. \quad (18)$$

We can see that

$$\lim_{z \rightarrow 1} \tilde{g}(s, z) = \lim_{y \rightarrow 0} \tilde{g}_{exp}(s, y) = \frac{1}{s},$$

and it is elementary to show that the generating function

$$g(t, z) = \hat{\mathcal{L}}^{-1} \{ \tilde{g}(s, z) \},$$

where $\hat{\mathcal{L}}^{-1}$ is the operator of the inverse Laplace transformation, satisfies the equation

$$\frac{\partial g(t, z)}{\partial t} = -h_0 (1 - z) g(t, z) - \alpha (n_c - 1) z (1 - z) \frac{\partial g(t, z)}{\partial z} + \alpha z^2 (1 - z) \frac{\partial^2 g(t, z)}{\partial z^2}, \quad (19)$$

with

$$g(0, z) = 1, \quad \text{and} \quad g(t, 1) = 1.$$

Similarly, the exponential generating function

$$g_{exp}(t, y) = \hat{\mathcal{L}}^{-1}\{\tilde{g}_{exp}(s, z)\}$$

is nothing else then the solution of the equation

$$\frac{\partial g_{exp}(t, y)}{\partial t} = -h_0(1 - e^y) g_{exp}(t, y) - \alpha n_c(1 - e^y) \frac{\partial g_{exp}(t, y)}{\partial y} + \alpha(1 - e^y) \frac{\partial^2 g_{exp}(t, y)}{\partial y^2}, \quad (20)$$

with

$$g_{exp}(0, y) = 1, \quad \text{and} \quad g_{exp}(t, 0) = 1.$$

A. Expectation value

The numbers of particles X and A at time instant $t \geq 0$ are given by

$$\xi_X(t) = N_X + \xi(t), \quad \text{and} \quad \xi_A(t) = N_A - \xi(t),$$

respectively. From these one obtains

$$\mathbf{E}\{\xi_X(t)\} = m_X(t) = N_X + \mathbf{E}\{\xi(t)\} \quad (21)$$

$$\mathbf{E}\{\xi_A(t)\} = m_A(t) = N_A - \mathbf{E}\{\xi(t)\}, \quad (22)$$

where

$$\mathbf{E}\{\xi(t)\} = m_1(t) = \left[\frac{\partial g(t, z)}{\partial z} \right]_{z=1} = \left[\frac{\partial g_{exp}(t, y)}{\partial y} \right]_{y=0}. \quad (23)$$

By using the equation (20) after elementary algebra we obtain

$$\frac{dm_1(t)}{dt} = h_0 + \alpha n_c m_1(t) - \alpha m_2(t), \quad (24)$$

where

$$m_2(t) = \mathbf{E}\{\xi^2(t)\},$$

and this equation can be rewritten in the form:

$$\frac{dm_1(t)}{dt} = \alpha [N_A - m_1(t)] [N_X + m_1(t)] - \alpha \mathbf{D}^2\{\xi(t)\}. \quad (25)$$

As seen the appearance of the variance $\mathbf{D}^2\{\xi(t)\}$ brings about the loss of validity of the *kinetic law of the mass action*. If $\mathbf{D}^2\{\xi(t)\} \approx 0$, i.e. if $m_2(t) \approx [m_1(t)]^2$, then the deterministic kinetic equation can be applied.

The equation (24) shows the hierarchical structure of momentum equations. If we would like to calculate $m_1(t)$ by solving the equation (24), we see that for this we need the second moment $m_2(t)$. The equation of the second moment contains the third moment etc. In this way we can obtain the time dependence of the average number of X particles $m_1(t)$ when we solve the hierarchical system of equations which seems to be rather difficult. Therefore, in the practice the *method of decoupling*¹ has been often used for finding an "approximate" solution, however the consequences of this procedure were hardly investigated. In the next Section we try to give some elementary analysis of the problem.

¹ The decoupling is the substitution of the moment $m_k(t)$ with an expression containing moments with indices smaller than k .

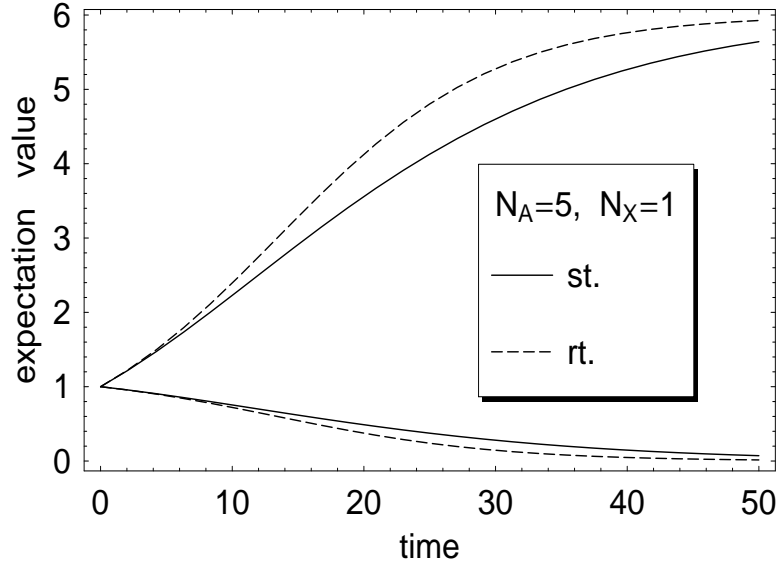


FIG. 2: Expectation values of the relative numbers of particles of type X (upper curves) and of type A (lower curves) versus time provided that the initial state of the system was $\{5, 1\}$.

In the present case it is fortunate that we can determine the probabilities $p(t, n)$, $n = 0, 1, \dots, N_A$ from (11), and so we can calculate directly *the exact time dependence of moments*

$$m_k(t) = \mathbf{E}\{[\xi(t)]^k\} = \sum_{n=0}^{N_A} n^k p(t, n). \quad (26)$$

The expectation values of the relative numbers of X and A particles, i.e. the mean values of the random functions

$$\rho_X(t) = 1 + \frac{\xi(t)}{N_X}, \quad \text{and} \quad \rho_A(t) = 1 - \frac{\xi(t)}{N_A}$$

versus time can be seen in FIG. 2. The upper curves refer to the X , while the lower curves to the A particles. The continuous and dashed curves show the results of calculations for the stochastic and deterministic models, respectively. As expected the difference between the stochastic and deterministic description is relatively small at the beginning and at the end of the process.

B. Variance

We have seen that the occurrence of the variance $\mathbf{D}^2\{\xi(t)\}$ in the differential equation of (25) is the source of the invalidity of the kinetic law of the mass action. Therefore, it seems to be worthwhile to look at the time dependence of the variance and relative variance of the number of X particles.

Since $\xi_X(t) = N_X + \xi(t)$ and $\xi_A(t) = N_A - \xi(t)$, it is trivial that

$$\mathbf{D}^2\{\xi_X(t)\} = \mathbf{D}^2\{\xi_A(t)\} = \mathbf{D}^2\{\xi(t)\},$$

where

$$\mathbf{D}^2\{\xi(t)\} = \sum_{n=0}^{N_A} [n - m_1(t)]^2 p(t, n).$$

By using the inverse Laplace transform of the expression (11), we can calculate the variance $\mathbf{D}^2\{\xi(t)\}$. The results of calculations are plotted in FIG. 3. Observe, the increase of the number of starting X particles from 1 to 3

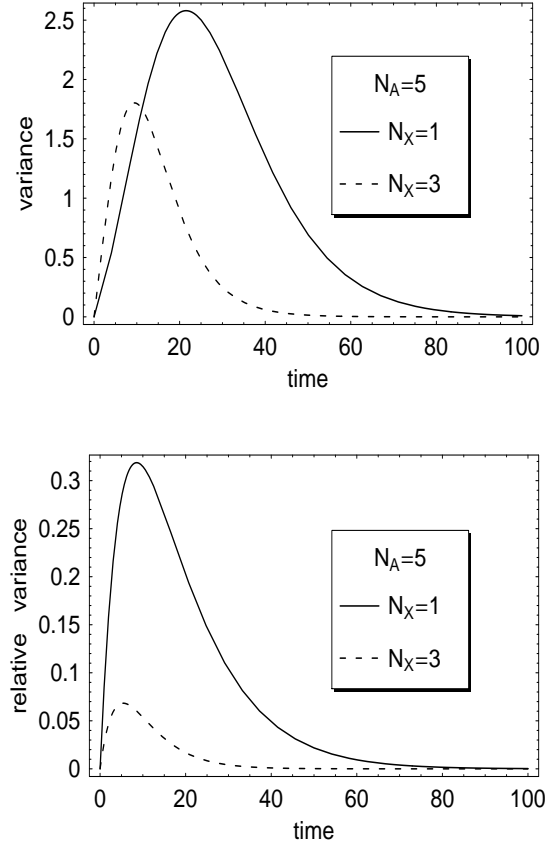


FIG. 3: Time dependence of the variance $\mathbf{D}^2\{\xi_X(t)\}$ and the relative variance $\mathbf{D}^2\{\xi_X(t)\}/\mathbf{E}^2\{\xi_X(t)\}$ in two initial states: $\mathcal{S}_0 = \{5, 1\}$, $\{5, 3\}$.

brings about a significant decrease of the relative variance. The fluctuation of $\xi(t)$ increases sharply at the beginning of the process, and decreases slowly with increasing time. After elapsing a sufficiently large time we see that the fluctuation is negligible, and it means that the kinetic rate equation can be regarded in long time limit as an acceptable approximation.

III. MOMENT-CLOSURE APPROXIMATION

In order to show the consequences of heuristic methods applied often for obtaining an "approximate" solution of the hierarchical equation systems, let us derive the exact equations for $m_1(t)$ and $m_2(t)$. It follows from (20) that

$$\frac{dm_1(t)}{dt} = h_0 + \alpha n_c m_1(t) - \alpha m_2(t) \quad (27)$$

and

$$\frac{dm_2(t)}{dt} = h_0 + (2h_0 + \alpha n_c) m_1(t) - \alpha(2n_c - 1) m_2(t) - 2\alpha m_3(t). \quad (28)$$

We see that further equations are needed for $m_3(t), m_4(t), \dots$, and this makes the problem rather complex, however, the stationary values $m_k^{(st)} = \lim_{t \rightarrow \infty} m_k(t)$, $k = 1, 2, \dots$ can be easily obtained. Since $m_1^{(st)} = N_A$, from (27) it follows that $m_2^{(st)} = N_A^2$, and by induction it can be proved that

$$m_k^{(st)} = N_A^k, \quad k = 1, 2, \dots$$

If we would like to determine the time dependence of the mean value $m_1(t)$, then we should solve the hierarchial system of moment equations. The usual treatment of this problem is to use the moment-closure approximation, i.e. to truncate the hierarchical equation system. However, this procedure may bring about hardly foreseeable consequences.

For example, if we substitute $m_3(t)$ in Eq. (28) with the product $m_1(t) m_2(t)$, then we obtain two differential equations for $m_1(t)$ and $m_2(t)$, namely ²

$$\frac{dm_1(t)}{dt} = h_0 + \alpha n_c m_1(t) - \alpha m_2(t),$$

and

$$\frac{dm_2(t)}{dt} = h_0 + (2h_0 + \alpha n_c) m_1(t) + \alpha(2n_c - 1) m_2(t) - 2\alpha m_1(t) m_2(t).$$

Eliminating $m_2(t)$ in the second equation we can write that

$$\frac{d^2 m_1(u)}{du^2} + 2n_c[N_A - m_1(u)] [N_X + m_1(u)] + (1 - 3n_c) \frac{dm_1(u)}{du} + 2m_1(u) \frac{dm_1(u)}{du} = 0, \quad (29)$$

where $u = \alpha t$. We have to solve this equation, by taking into account the initial conditions

$$m_1(0) = 0, \quad \text{and} \quad \left[\frac{dm_1(u)}{du} \right]_{u=0} = N_A N_X. \quad (30)$$

For the sake of simplicity we assume that $N_A = N_X = M$, i.e. $n_c = 0$. In this case we obtain

$$\frac{d}{du} \left(\frac{dm_1}{du} + m_1 + m_1^2 \right) = 0.$$

It follows from this

$$\frac{dm_1}{du} + m_1 + m_1^2 = C,$$

where C can be determined by applying the conditions (30). As seen, $C = M^2$, and so we have

$$\frac{dm_1}{du} = -(m_1^2 + m_1 - M^2),$$

the solution of which is given by

$$m_1(u) = 2M^2 \frac{1 - e^{-\lambda_M u}}{\lambda_M(1 + e^{-\lambda_M u}) + 1 - e^{-\lambda_M u}}, \quad (31)$$

where $\lambda_M = \sqrt{4M^2 + 1}$. The first thing that can be seen immediately is

$$\lim_{u \rightarrow \infty} m_1(u) = M \frac{1}{\sqrt{1 + 1/(2M)^2} + 1/2M},$$

and this limit value does not correspond to the exact relation $\lim_{u \rightarrow \infty} m_1(u) = M$.

In the upper part of FIG. 4 we plotted the exact "ex" and approximate "cl" values of $\mathbf{E}\{\rho_X(u)\}$ versus $u = \alpha t$, and for the sake of comparison the curve "rt" obtained from Eq.(4) is also plotted. It is remarkable that the decoupling $m_3(t) \approx m_1(t)m_2(t)$ brings about larger error than the rate equation (4) which corresponds to the decoupling $m_2(t) \approx m_1(t)m_1(t)$. As seen, the difference between the curves "ex" and "cl" vs. u is negligible at the beginning and at the end of the process. The lower part of FIG. 4 shows the time dependence of the differences between the curves "ex"

² Though these equations are different from the exact equations (27) and (28), for the sake of simplicity, we are using the same notations for the approximate first and second moments.

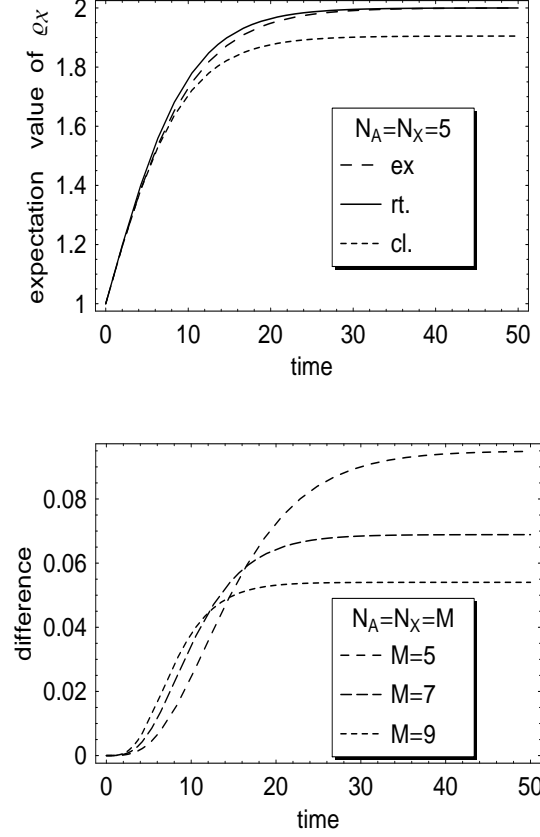


FIG. 4: In the upper part the time dependence of $\mathbf{E}\{\rho_X(u)\}$ calculated by exact "ex" and approximate "cl" methods is shown. For the sake of comparison the curve "rt" obtained from Eq.(4) is also plotted. In the lower part the difference between the curves "ex" and "cl" vs. $u = \alpha t$ is shown for three values of M .

and "cl" for three values of M . Note, the difference decreases sharply with increasing M . Summarizing, we can state that the decoupling $m_3(t) \approx m_1(t) m_2(t)$ brings about an unacceptable error in the calculation of $m_1(t)$.

However, there is an other way to truncate the hierarchical equation system. We can calculate the cumulants of $\xi(t)$ from the derivatives of $K(t, y) = \log g_{exp}(t, y)$ at $y = 0$. As known, the cumulants

$$\kappa_k(t) = \left[\frac{\partial^k K(t, y)}{\partial y^k} \right]_{y=0}$$

are zero in the case of normal distribution if $k \geq 3$. Although the random function $\xi(t)$ does not follow the normal distribution at any $t \geq 0$, in contrary to this we assume that $\kappa_3(t) = 0$, and hence we use the following decoupling:

$$m_3(t) \approx 3m_2(t)m_1(t) - 2m_1^3(t). \quad (32)$$

This closure is called by some authors [6] "normal approximation". In order to simplify the calculations, we are dealing with the case when $N_A = N_X = M$. By using the expression (32), we obtain from (27) and (28) the equations

$$\frac{1}{\alpha} \frac{dm_1(t)}{dt} = M^2 - m_2(t)$$

and

$$\frac{1}{\alpha} \frac{dm_2(t)}{dt} = M^2 - m_2(t) [1 + 6m_1(t)] + 2m_1(t)[M^2 + 2m_1^2(t)],$$

As expected, one can easily show that the stationary stable solution is $m_1^{(st)} = M$. The time dependence has been calculated numerically. FIG. 5 shows the dependence of the difference between the exact and the "normal"

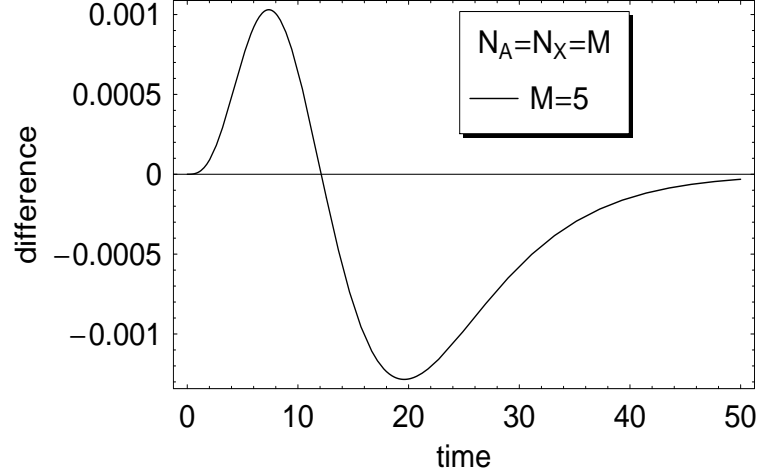


FIG. 5: Dependence of the difference between the exact and approximate solutions on $u = \alpha t$. The approximate solution corresponds to the closure $\kappa_3(t) = 0$.

approximate solutions on $u = \alpha t$. One can observe that the difference is surprisingly small even if few particles ($M = 5$) are participating in the process, however one cannot conclude that the closure $\kappa_3(t) = 0$ is always the best.

IV. LIFETIME OF THE SYSTEM

Assume that the *system* \mathcal{S} is "live" when it contains at least 1 particle of type X and the number of particles A is larger than zero. In the course of the process the X particles are converting the A particles into X particles until A particles can be found in the system. Denote by θ that random moment when the last A particle is converted into X . The random variable θ is called *lifetime of the system* \mathcal{S} . It is obvious that the event $\{\theta \leq t\}$ is equivalent to the event $\{\xi(t) = N_A | \mathcal{S}_0\}$, where N_A and N_X are larger than zero. Consequently

$$\mathcal{P}\{\theta \leq t | \mathcal{S}_0\} = W(t | \mathcal{S}_0) = \mathcal{P}\{\xi(t) = N_A | \mathcal{S}_0\} = p(u, N_A | \mathcal{S}_0) \quad (33)$$

is the probability that the lifetime of the system \mathcal{S} is not larger than t provided that the initial state of the system was $\mathcal{S}_0 = \{N_A, N_X\}$. We can see that the properties of the system lifetime are determined by the probability $p(t, N_A)$.³ The probability density function of the lifetime is nothing else than

$$w(t | \mathcal{S}_0) = \frac{dp(t, N_A)}{dt}, \quad (34)$$

and we can see that

$$\int_0^\infty e^{-st} w(t | \mathcal{S}_0) dt = \tilde{w}(s | \mathcal{S}_0) = s U_{N_A}(s), \quad (35)$$

since $p(0, N_A) = 0$, if $N_A \neq 0$. By using the formula (11) one obtains

$$\tilde{w}(s | \mathcal{S}_0) = \frac{h_0 h_1 \cdots h_{N_A-1}}{(s + h_0)(s + h_1) \cdots (s + h_{N_A-1})}, \quad (36)$$

and it is evident that

$$\tilde{w}(0 | \mathcal{S}_0) = \int_0^\infty w(t | \mathcal{S}_0) dt = 1.$$

³ Here we omitted the notation referring to the initial state.

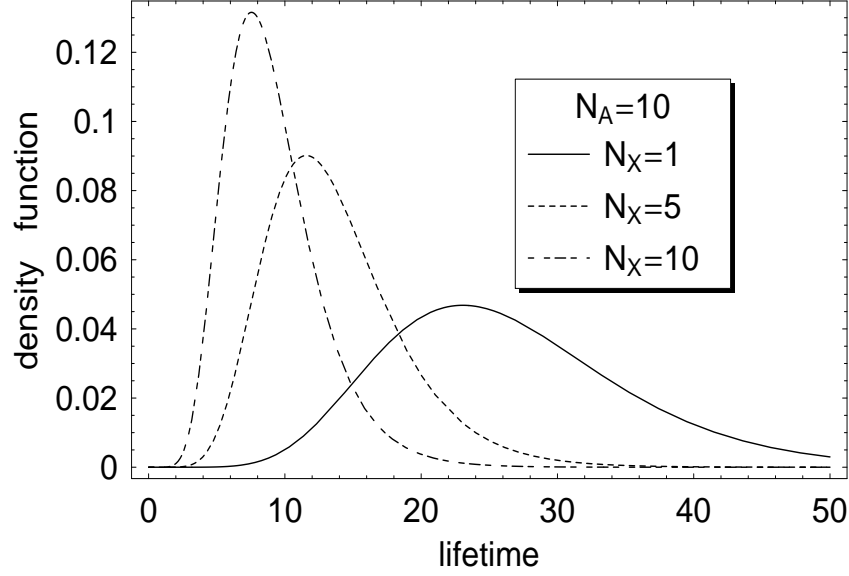


FIG. 6: Probability density function of the lifetime for three initial states: $\{10, 1\}$, $\{10, 5\}$ and $\{10, 10\}$.

It can be worthwhile to study the temporal behavior of systems containing at $t = 0$ only 1 particle of type X and $N_A > 1$ of type A , i.e. to follow the process from the initial state $\mathcal{S}_0 = \{N_A, 1\}$ to the dead state $\mathcal{S}_d = \{0, N_A + 1\}$. Since in this case $N_A = n_c + 1$ and $N_X = 1$, if $n_c = 2k_c$, where k_c is a nonnegative integer, then we obtain

$$\tilde{w}(s|\mathcal{S}_0) = \left[\frac{h_0 h_1 \cdots h_{k_c}}{(s + h_0)(s + h_1) \cdots (s + h_{k_c})} \right]^2,$$

while if $n_c = 2k_c + 1$, then we can write

$$\tilde{w}(s|\mathcal{S}_0) = \left[\frac{h_0 h_1 \cdots h_{k_c}}{(s + h_0)(s + h_1) \cdots (s + h_{k_c})} \right]^2 \frac{h_{k_c+1}}{s + h_{k_c+1}}.$$

In order to calculate the probability density function of the lifetime at different initial states, we should determine the inverse Laplace transforms of these expressions. In FIG. 6 we see three probability density functions of the lifetime θ belonging to initial states: $\mathcal{S}_0 = \{10, 1\}$, $\{10, 5\}$ and $\{10, 10\}$. It is remarkable that at fixed initial number of A particles the most probable lifetime of the system decreases significantly with increasing initial number of X particles.

For the sake of determination of the expectation value $\mathbf{E}\{\theta\}$ and the variance $\mathbf{D}^2\{\theta\}$ of the system lifetime θ define the function

$$K(s|\mathcal{S}_0) = \log \tilde{w}(s|\mathcal{S}_0) = \sum_{n=0}^{N_A-1} \log \frac{h_n}{s + h_n}. \quad (37)$$

We obtain immediately that

$$\mathbf{E}\{\theta|N_A, N_X\} = - \left[\frac{dK(s|N_A, N_X)}{ds} \right]_{s=0} = \sum_{n=0}^{N_A-1} \frac{1}{h_n}, \quad (38)$$

and

$$\mathbf{D}^2\{\theta|N_A, N_X\} = \left[\frac{d^2 K(s|N_A, N_X)}{ds^2} \right]_{s=0} = \sum_{n=0}^{N_A-1} \frac{1}{h_n^2}. \quad (39)$$

By using these formulas we calculated the ratios

$$\frac{\mathbf{E}\{\theta|N_A, N_X\}}{\mathbf{E}\{\theta|1, 1\}}, \quad \text{and} \quad \frac{\mathbf{D}^2\{\theta|N_A, N_X\}}{\mathbf{D}^2\{\theta|1, 1\}}$$

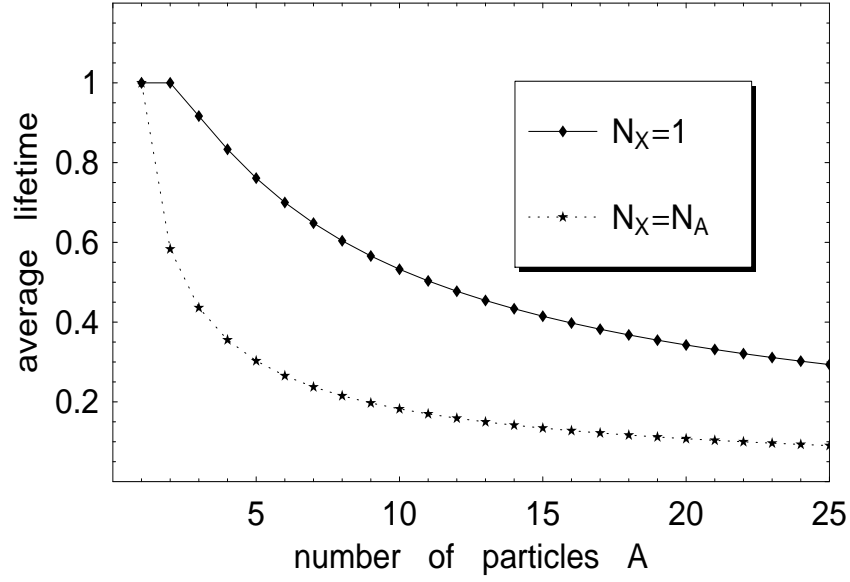


FIG. 7: Dependence of the average lifetime of the system \mathcal{S} on the initial number of A particles in the cases of $N_X = 1$ and $N_X = N_A$.

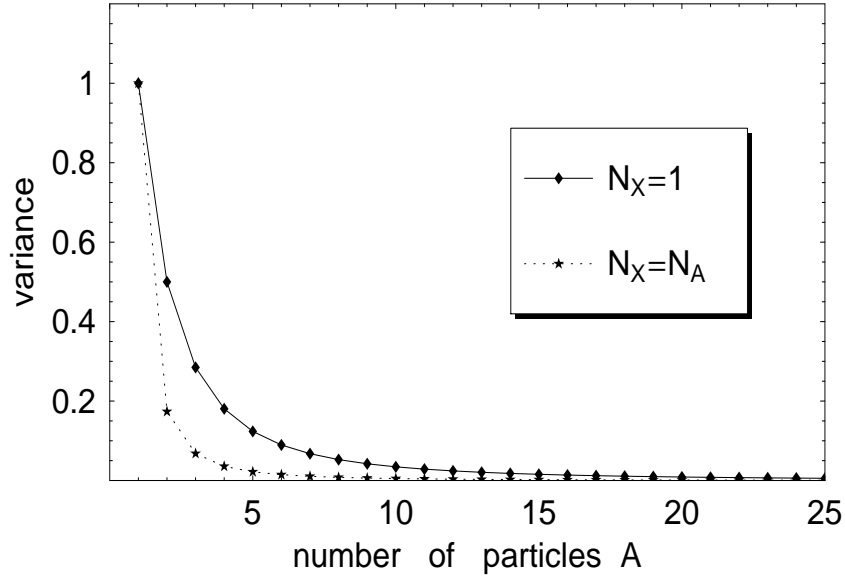


FIG. 8: Dependence of the variance of the lifetime on the initial number of A particles in the cases of $N_X = 1$ and $N_X = N_A$.

and plotted them in FIG. 7 and FIG. 8.

At the first moment it is surprising that the increase of the initial number of A particles results in a decrease of the expectation value and the variance of the system lifetime. It seems to be true that could be happened in the folktale: the "large" disappears faster than the "small". In fact, the larger is the initial number of A particles the faster is the autocatalytic reaction, and this explains that we see in figures.

V. CONCLUSIONS

The main purpose of this paper was to study the stochastic properties of small systems controlled by autocatalytic reaction. In order to give exact solution of the problem we assumed the distribution of reacting particles in the system volume to be uniform and introduced the notion of *the point model of reaction kinetics*. In this model the probability of a reaction between two particles per unit time is evidently proportional to the product of their actual numbers. For the sake of simplicity we used in this paper the notations X and A for *the autocatalytic and the substrate particles*, respectively.

In order to make the calculations not very complex we have chosen the simplest autocatalytic reaction: $A + X \rightarrow 2X$, and constructed a stochastic models for it. The *state of the system* at a given time moment is completely determined by the actual numbers of X and A particles. The system is called *living* at time $t \geq 0$ when the probability of the autocatalytic reaction is larger than zero.

We *calculated exactly* the probability $p(t, n)$ of finding n new X particles in the system at time moment t , provided that at $t = 0$ the number of new X particles was zero, and the system contained $N_X > 0$ particles of type X and $N_A > 0$ particles of type A . We have shown that the stochastic model results in an equation for the expectation value $m_1(t)$ of the new X particles which differs strongly from the kinetic rate equation. Consequently, we can state that in this case *the stochastic model does not support the kinetic law of the mass action*. It is to mention here that this statement was already published by Rényi [7] many years ago. We calculated the difference between the time dependencies of mean values corresponding to the stochastic and the deterministic models.

Moment-closure approximations of two types have been analyzed, and the results of calculations were compared with the exact mean values obtained directly from the probabilities $p_n(t)$, $n = 0, 1, \dots$. We found that the "normal" approximation which neglects the third and higher order cumulants can be accepted as relatively "good" approximation.

The probability density function of *the system lifetime* has been also calculated, and it is found that the most probable lifetime depends sensitively on the number of X particles being present in the system at time moment $t = 0$.

The main conclusion is that *the point model of the stochastic reaction kinetics* resulted in a deeper understanding of the random behavior of small systems governed by autocatalytic processes.

-
- [1] S.A. Rice: *Diffusion-Limited Reactions*, (Elsevier, Amsterdam, 1985)
 - [2] E. Kotomin and V. Kuzovkov: *Modern Aspects of Diffusion-Controlled Reactions*, (Elsevier, Amsterdam, 1996)
 - [3] C.W. Gardiner: *Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences*, (Springer, Berlin, 1983)
 - [4] N.G. Van Kampen: *Stochastic Processes in Physics and Chemistry*, (Elsevier, Amsterdam, 2004)
 - [5] P. Whittle, J. Roy. Statist. Soc., **B19**, 268 (1957)
 - [6] K. Nishiyama, Journal of the Physical Society of Japan, **37**, 44 (1974)
 - [7] A. Rényi: Publications de l'Institut des Mathématiques Appliquées de l'Academy des Sciences de Hongrie. **2**, 93 (1954)